CONTRIBUTIONS

TO OUR

KNOWLEDGE OF PHENUVINIC ACID

AND

PHENYLKETOPENTENE.

INAUGURAL DISSERTATION

OF THE MATHEMATICAL AND NATURAL SCIENCE FACULTY

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SUBMITTED BY

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I would take this opportunity of thanking Professor Fittig, for the many kindnesses he showed me, during my stay in Strassburg.

PHENUVINIC ACID

SYNTHETICAL PREPARATION.

CONSIDERATIONS

OF ITS RELATIONSHIP WITH PHENYL METHYL

FURFURAN CARBOXYLIC ACID.

INTRODUCTION.

Schloesser[1] by a reaction exactly analagous to one, which in the hands of v. Eynern had yielded Methronic Acid, and also to one which had afforded Dietzel the means of preparing the next homologue, prepared an acid, the corresponding representative of Methronic Acid in the Aromatic Series, which on the suggestion of Professor Fittig, he named Phenythronic Acid. Its method of production rested on the condensation taking place between, Sodium Succinate and Benzoyl Acetic Ether in the presence of Acetic Anhydride.

$$C_9H_8(C_2H_5)O_3 + C_4H_6O_4 = C_{13}H_9(C_2H_5)O_5 + 2\ H_2O.$$

This acid, a dibasic acid, yields by elimination of Carbonic Acid from one of its Carboxyl groupings, a monobasic Acid, Phenuvinic Acid. From the comparison of the salts of Harrows[2] Pyrotritaric Acid, and of the acid obtained by v. Eynern, by elimination of Carbon dioxide from Methronic Acid, Paul Feist established the identity of these acids. Hence Phenuvinic Acid is the representative in the aromatic series of Harrow's Pyrotritaric Acid, just as Phenythronic Acid is the aromatic analogue of Methronic Acid.

Fittig[3], who regards the products of the condensation of a Ketonic Acid with Sodium Succinate in the presence of

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1 Ann. 250, 212.
2 Ann. 201, 141.
3 Ber. 21, 2133.

Acetic Anhydride, as Tetrylene derivatives, gave the following theoretical interpretation of Schloesser's reaction,

$$\begin{array}{l} C_6H_5 . CO \\ \quad | \\ C_2H_5 . O . OC . CH_2 \end{array} + \begin{array}{l} CH_2 . CO . OH \\ \quad | \\ CH_2 . CO . OH \end{array} = \begin{array}{l} C_6H_5 . C(OH) . CH . CO . OH \\ \quad | \qquad\quad | \\ C_2H_5 . O\,OC . CH_2 \quad CH_2 . CO . OH \end{array}$$

$$= \begin{array}{l} \qquad\qquad C_6H_5 . C{-}CH . CO . OH \\ \qquad\qquad\quad \| \quad | \\ C_2H_5 . O . OC . C \quad CH_2 \\ \qquad\qquad\quad \diagdown \diagup \\ \qquad\qquad\quad CO \end{array} + 2\,H_2O$$

and assigned to Phenuvinic Acid the formula,

$$\begin{array}{l} C_6H_5 . C{-}CH . CO . OH \\ \qquad\quad \| \quad | \\ \qquad HC \quad CH_2 \\ \qquad\quad \diagdown \diagup \\ \qquad\quad CO \end{array}$$

Paal[1] had obtained, by the action of the Sodium Compound of Aceto. Acetic Ether upon Brom-Acetophenone, an ether which by susequent splitting off of the elements of water, effected through the agency of Hydrochloric Acid, yielded the ether of an acid, which he regarded as Phenyl Methyl Furfuran Carboxylic Acid. By a precisely similar method Paal succeeded in preparing Pyrotritaric Acid, to which acid and to the acid obtained as above, he gave the formulae

$$\begin{array}{l} C_6H_5 . C{-}O{-}C . CH_3 \\ \qquad\quad \| \qquad \| \\ \qquad HC{-}\!\!-\!\!-C . CO . OH \end{array}$$

Phenyl Methyl Furfuran Carboxylic Acid.

$$\begin{array}{l} CH_3 . C{-}O{-}C . CH_3 \\ \qquad\quad \| \qquad \| \\ \qquad HC{-}\!\!-\!\!-C . CO . OH \end{array}$$

Pyrotritaric Acid.

Fittig did not accept the constitution of Paal for the acid discovered by the last named chemist, but regarding it as an isomer of Phenuvinic Acid, assigned to it an analagous formula, and interpreted the reaction of Paal as follows,

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[1] Ber. 16, 2865.

$$C_6H_5 . CO . CH_2Br + CH_3 . CO . CHNa . CO\,OC_2H_5 = NaBr + C_6H_5 . CO . \underset{\displaystyle CH_3 . CO . CH . CO . OC_2H_5}{\underset{|}{CH_2}}$$

$$\underset{\displaystyle CH_3 . CO . CH . CO . OC_2H_5}{\underset{|}{C_6H_5 . CO . CH_2}} = H_2O + \underset{\displaystyle \quad\quad CO}{\overset{\displaystyle HC \quad CH . CO . OC_2H_5}{\overset{\displaystyle \| \quad |}{C_6H_5 . C - CH_2}}}$$

If the relationship between the acids of Paal and of Schloesser be such as Fittig proposes, whether they possess the constitution assigned to them by Paal, or the one accepted by Fittig, a method analogous to the one by which Paal prepared his acid, should yield the acid of Schloesser. Accordingly Chloracetone reacting with the Sodium Compound of Benzoyl Acetic Ether should give, by subsequent elimination of the elements of water and saponification of the resulting ether, Schloesser's Acid.

SYNTHETIC PREPARATION OF PHENUVINIC ACID.

At the suggestion of Professor Fittig, I undertook the examination of the reaction suggested by the above theoretical considerations.

In the preparation of the Sodium Compound of Benzoyl Acetic Ether, 3,6 grms of Sodium, carefully freed from adhering oil, were dissolved in Alcohol, in a flask provided with a reflux condenser closed by a Calcium Chloride tube. The weight of the Alcohol taken was ten to twelve times the weight of the Sodium, and in the experiments only Alcohol was used, which had been distilled over lime, and then rendered absolute by further distillation over Sodium. To the cold alcoholic solution of Sodium Ethylate, 30 grms. of Benzoyl Acetic Ether, boiling between 168° and 172° under a pressure of 20 mm.,[1]

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[1] C. f. Claissen, Ber. 20, p. 651.

were added, drop by drop with vigorous shaking. After the addition of the Ether was complete, the mixture was gently heated on the water-bath for a few minutes until the Alcohol began to distil. Throughout the whole operation great care was taken to prevent the ingress of moisture from the air.

Acetophenone Benzoyl Acetic Ether: This the theoretically resulting product of the second stage of the reaction was prepared as follows. The theoretical quantity of pure Chloracetone, boiling between 118,5°—119° C., namely 14,4 grms., was added drop by drop to the Alcoholic solution of Sodium Benzoyl Acetic Ether. No rise of temperature was noticeable, but the separation of Sodium Chloride proceeded in the cold. The reaction was furthered by half an hour's gentle heating on the water-bath, an increased precipitation of Sodium Chloride being noticed. Eventually the alcohol was evaporated off and the ether separated by water. After the solution of the Sodium Chloride was complete, the product of the reaction was shaken out with alcohol-free ether. An analysis of the resulting ether, which had stood several days over Sulphuric Acid in vacuo, gave,

. 1275 substance gave . 0785 H_2O . 3045 CO_2

C = 65,13		67,75	
	instead of		calculated for $C_{14}H_{16}O_4$
H = 6,82		6,45	

It would seem that, in contradistinction to what Paal found in his reaction, the product is impure. To effect the elimination of water from the product of the above reaction, the same was heated with dilute Hydrochloric Acid. In one experiment, cold concentrated Hydrochloric Acid was used, but the ultimate yield of acid was pratically null. An acid of concentration 1 vol. HCl : 4 vols. H_2O was found to give the best results. With acid of this strength, the ether obtained as above, was heated for about an hour, and eventually the pro-

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[1] C. f. the corresponding stage in Paal's reaction.

duct distilled with steam. The distillate with steam was clearly divisible into two portions,

a) A portion, something like ninety °/₀ of the whole, distilling over very rapidly, and possessing the odour of Acetophenone.

b) A second fraction continuing to distil during many hours, and possessing a strong phenolic odour.

In addition, there always remained a quantity of resin which was boiled out with Barium Carbonate, and the evaporated solution tested for Phenuvinic acid, but only the slightest traces of a precipitate were formed with Hydrochloric Acid.

Each of the fractions of the distillate with steam was shaken out with ether, and after the ether had been evaporated off, gently warmed with alcoholic Potash. After the alcohol had been all got rid of on the water-bath, water was added, and in each case the solution was distilled with steam. In both cases it was found that something remained after treatment with alcoholic Potash, still volatile in steam. The fraction (a) seemed to have been entirely unattacked by the Alcoholic Potash, and after the second distillation with steam was found to boil completely between 190°—210°. From this, as a result of a second fractionation, a sample of pure Acetophenone boiling at 198° C. was obtained, which gave the following percentage composition on combustion,

. 2357 grms substance gave . 1426 H_2O, and . 6878 CO_2.

Calculated for C_8H_8O.	Found.
H = 6,66	6,71
C = 80,00	79,59

The portion still volatile in steam after heating fraction (b) with Alcoholic Potash, was found to distil between the temperatures 235°—240° C., or exactly those between which, according to Paal[1], the neutral body obtained by heating Acetophenone Acetone with Acetic Anhydride, distils. On cooling in

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[1] Ber. 17, p. 913.

a freezing mixture, crystals were obtained, which when pressed between filter paper, were found to melt at 38,5—39° C.

The agueous solutions, separated from everything volatile with steam, were neutralised with Hydrochloric Acid to a neutral or only sligtly alkaline reaction, and after clarifying with Animal Charcoal, were concentrated by evaporation. More Hydrochloric Acid was added, with the result that in the agueous solution obtained from fraction (b) a precipitate was formed, which on recrystallisation from alcohol, and careful drying over Sulphuric Acid in vacuo, gave,

. 2057 grms substance gave . 0937 H_2O and . 5358 CO_2

	Calculated	Theoretical for $C_{12}H_{10}O_3$
H	= 5,05	4,95
C	= 71,07	71,29

From the mother liquid after several days standing in the air, there was formed a second crop of crystals, bearing but little resemblance to the first. These crystals were much more soluble in water than those first deposited, and the aqueous solution was distinctly acid. The melting point was determined and found to lie between 119—120° C. From a portion of this second acid, which, as its melting point showed, was different to Schloesser's Acid, a Calcium salt was prepared. The analysis of the air-dried salt, gave

. 3128 grms substance gave . 0510 H_2O and . 1300 $CaSO_4$.

	Calculated	Theoretical for $(C_6H_5CO . O)_2 Ca . 3 H_2O$
H_2O	= 15,84	16,10
Ca	= 11,88	11,90

Hence this second crop of crystals was Benzoic Acid.

As a result, then, of heating the product of the reaction between Chloractone and Sodium Benzoyl Acetic Ether, with dilute Hydrochloric Acid, we have

a) Acetophenone formed in very large quantities.

b) An ester of an acid of the composition $C_{12}H_{10}O_3$.

c) Small quantities of a Neutral Body. M. P. 38,5-39° C.

In addition, we find crystallising out of the mother liquor, from which the acid of composition, $C_{12}H_{10}O_3$, has been precipitated, Benzoic Acid. Whether this acid is the result of the decomposition of unaltered Benzoyl Acetic Ether, or is formed in a later stage of the reaction, is not clearly demonstrated.

COMPARISON OF THE ACID, $C_{12}H_{10}O_3$, WITH SCHLOESSER'S PHENUVINIC ACID.

The melting point of a portion of the acid, which had been recrystallised from Alcohol, was taken, and found to lie between the temperatures 144—145° C. Schloesser[1] gives as the melting point of his acid, also the temperature 144—145° C. Moreover, a portion of the acid actually prepared by Schloesser and some of the acid I had obtained were compared, one and the same thermometer being used in each case, and found to melt at precisely the same temperature, namely, 144—145° C.

The solubility of the two acids was next examined. According to Schloesser, Phenuvinic Acid is insoluble in cold, and but difficulty soluble in boiling water. It is, however, easily soluble in Alcohol. The behaviour of the acid, I had obtained, was investigated, and was found in every case to correspond with Schloesser's statements as regards the solubility of Phenuvinic Acid.

As a further means of establishing the identity of the two acids, the Calcium salt of my acid was prepared. The salt was crystallised from its aqueous solution by standing over Sulphuric Acid in a vacuum. The crystals were filtered off and dried in the air. The analysis gave

. 2122 grms air dried salt lost at 160° C . 0160 H_2O and gave . 0266 grms CaO.

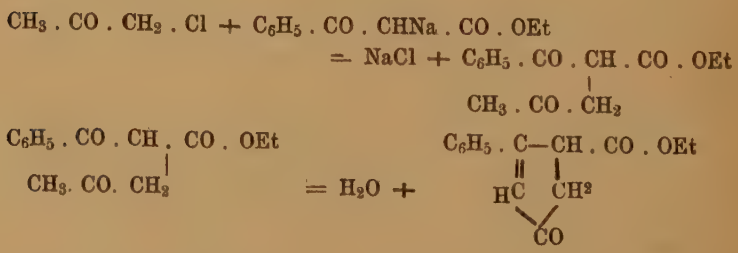
Calculated			Theoretical for $Ca(C_{12}H_9O_3)_2 . 2 H_2O$
Ca	=	8,95	9,05
H^2O	=	7,54	7,53

[1] Ann. 250, p. 220.

The Calcium Salt was prepared because of its characteristic solubility. Calcium Phenuvinate is according to Schloesser, not much more easily soluble in hot than in cold water. The Calcium Salt was found to possess a solubility in cold water but little inferior to that in hot, moreover, as in the case of Phenuvinate of Calcium, the salt lost all its water of crystallisation at 160° C.

By splitting Carbon dioxide off from Phenuvinic Acid, Schloesser[1] obtained a neutral body, with aromatic odour, and easily volatile with steam. The body possessed the melting point 40° C. A portion of the acid I had obtained, was distilled in a small bent tube, and the distillate warmed with Sodium Carbonate until all free acid was neutralised, and eventually distilled with steam. There passed over a body, with aromatic odour, and exceptionally volatile with steam, which deposited itself as an almost colourless oil. On removing a portion of the oil from the water, and setting it in a freezing mixture, long transparent needles were obtained, which after pressing between filter paper melted at 38,5—39° C.

Hence it would seem that the acid obtained as the result of the above reactions, and the acid obtained by Schloesser, and named by him Phenuvinic Acid, are identical. Its method of formation, accepting Fittig's formula for Phenuvinic Acid, may be explained.



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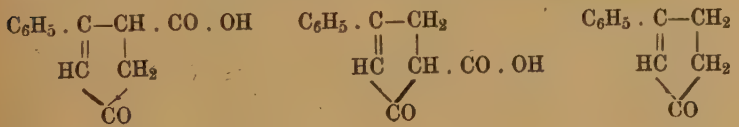
[1] Ann. 250, p. 222.

Hence Paal's Methyl Phenyl Furfuran Carboxylic Acid and Phenuvinic Acid are, as Fittig[1] suggested, isomeric. However, the above synthetical production of Phenuvinic Acid, though by its analogy to the method followed by Paal in the preparation of his Methyl Phenyl Furfuran Carboxylic Acid, shows the two acids to be isomeric, affords us no aid in distinguishing between the furfuran formula of Paal and the constitution assigned to them by Fittig.

PHENYLKETOPENTENE.

IDENTITY OF THE NEUTRAL BODIES RESULTING FROM PAAL'S AND SCHLOESSER'S ACIDS.

Schloesser[2], as previously stated, had obtained from Phenuvinic Acid by splitting off of Carbonic Acid, a neutral body $C_{11}H_{10}O$, with well defined properties, and melting at 40° C. From Phenyl Methyl Furfuran Carboxylic Acid, Paal[3] also had obtained by simple splitting off of Carbonic Acid, a neutral body, «Phenyl Methyl Furfuran.» From a comparison of the properties of these two bodies it would seem that they were identical, though Paal gave as the melting point of his Phenyl Methyl Furfuran 41—42° C. Theoretically the isomerism of Phenyl Methyl Furfuran Carboxylic Acid, and Phenuvinic Acid, necessitates the identity of the two neutral bodies resulting from the acids by elimination of Carbon dioxide.



or according to Paal,

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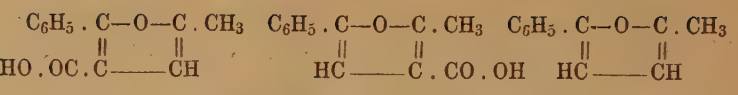
[1] Ber. 21, p. 2135.
[2] Ann. 250. p. 222.
[3] Ber. 17, 915 and 2759.



With a view to establishing their identity, I prepared some of Paal's acid, and, after recrystallising from alcohol, analysed the acid, melting 178—179° C.:

. 2180 grms gave . 1043 grms H_2O . 5681 CO_2.

	Calculated	Theoretical for $C_{12}H_{10}O_3$
H	= 5,31	4,95
C	= 71,07	71,29

From this acid, possessing as it did, the molecular weight $C_{12}H_{10}O_3$, as well as from a portion of the Phenuvinic Acid, which by melting point determination, and analysis, I had shown to be pure, I obtained by dry distillation the two neutral bodies, and after distilling in steam, and purifying the crystals by pressing between filter paper, examined their melting points. The determinations were made with one and the same thermometer.

The neutral body resulting from Phenuvinic Acid melted at 38,5—39° C.

The neutral body obtained from Paal's acid melted also at the same temperature 38,5—39° C.

A portion of the product from Schloesser's acid crystallised with a crystal of the second neutral body possessed exactly the same melting point.

As a difference in melting point was practically the only want of agreement between the properties of these two bodies, as described by their respective discoverers, they may now be taken to be identical, and therefore in perfect agreement with the predictions of theory.

PREPARATION OF METHYL PHENYL FURFURAN CARBOXYLIC ACID; COMPARISON OF THE REACTIONS BETWEEN SODIUM ACETO-ACETIC ETHER AND BROMACETOPHENONE, AND BETWEEN SODIUM BENZOYL ACETIC ETHER AND CHLORACETONE.

With a view to more fully investigate the Neutral Body, «Phenylketopentene», resulting alike from Phenuvinic Acid and from Paal's acid, I determined to try whether this latter acid was not more easily obtainable than Phenuvinic Acid. Schloesser[1] obtained a yield of but 5% on his Phenythronic Acid. I myself never obtained a better yield than about four per cent of Phenuvinic Acid, as prepared from Chloracetone and Sodium Benzoyl Acetic Ether. Accordingly, Paal[2] having stated that his acid was obtainable when Acetophenone Aceto-acetic Ether was heated with aqueous Hydrochloric Acid, and the resulting ether saponified, this method of preparation was followed. Bromacetophenone was prepared according to the method of Möhlan[3] which was found to give better results, the product becoming more easily solid and being lighter coloured, than were obtainable with Staedel's[4] method. To a solution in alcohol of Sodium Ethylate, corresponding in quantity to 3,5 grms of Sodium, 20 grms of Aceto-Acetic Ether were added drop by drop, and the mixture heated for a few minutes on the water-bath. After careful cooling in ice-cold water, 30 grms of Bromacetophenone were introduced. The addition of the Bromacetophenone was invariably attended with very considerable heat evolution, and the precipitation of Sodium Bromide proceeded almost from the moment of introducing the same. The Acetophenone Aceto-Acetic Ether so obtained, after separation from Alcohol and Sodium Bromide, was heated with aqueous Hydrochloric Acid of concentration, 1 vol. of concen-

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[1] Dissertation p. 6.
[2] Ber. 17, p. 913.
[3] Ber. 15, 2464.
[4] Ber. 13, 837.

trated acid : five vols. of water, for about two hours, and the product eventually distilled with steam. The whole product distilled continuously throughout many hours, and no fraction, distilling rapidly with steam, could be separated, as in my own reaction, though after a time the odour of the Neutral Body was noticeable. After shaking out with ether, the ester was saponified, and the acid precipitated from the aqueous solution of its Potassium salt with Hydrochloric Acid. Recrystallised from Alcohol, the acid possessed the melting point 178—179° C., and the yield, (15 grms) represented approximately 50 % of the theoretical.

Exactly as in my own reaction there remained, after saponification, something unattacked by Caustic Potash, so here after saponification there still remained a part volatile with steam. This was fractionated, with the result that two distinct substances were obtained.

a) A fraction boiling 235—240° C., which on cooling solidified and gave crystals of the Neutral Body melting 38,5—39° C.

b) A fraction distilling over, 310—312° C., which became only partly solid and was not further investigated.

Practically no Acetophenone had been formed.

It is impossible to say how far the Acetophenone, formed in my reaction, was the product of the decomposition of unaltered Benzoyl Acetic Ether, but one may certainly say, that of the two ethers, so closely allied in composition ;

$$C_6H_5 . CO . CH^2 \qquad\qquad C_6H_5 . CO . CH . CO . OC_2H_5$$
$$\qquad\quad | \qquad\qquad\qquad\qquad\quad |$$
$$CH_3 . CO . CH . CO . OC_2H_5 \qquad CH_3 . CO . CH_2$$

the ease with which they are formed by reactions, strictly analogous, is very different in the two cases, or else that the one lends iself to a splitting off of the elements of water of an appreciably complete nature, while the other suffers very considerable decomposition with the formation of Acetophenone.

PREPARATION OF THE NEUTRAL BODY.

Schloesser[1] obtained Phenylketopentene by distilling Phenythronic Acid, Phenuvinic Acid being also largely present in the distillate. In an exactly similar manner Paal's acid was distilled in small bent tubes, one end being blown out into a bulb, and after warming with a solution of Sodium Carbonate, to take up the unaltered acid, the neutral body was distilled off in steam. It was found that a larger quantity of acid became converted into neutral body, when the acid was heated for some considerable time above its melting point without actually allowing it to distil. 20 grms of pure acid so distilled. yielded 12,7 grms pure neutral body, or a yield of 81 % of the theoretical quantity. The recovered acid was of course continually redistilled until completely converted into neutral body. The Phenylketopentene was invariably crystallised by withdrawing a small portion of the oil from the watery distillate, cooling until it solidified, and then introducing a crystal into the remaining portion, when the whole became solid and could be easily filtered off from the water. In every case before using any of the neutral body for experiments, its melting point was taken as a test of its purity.

DETERMINATION OF THE BOILING POINT OF THE NEUTRAL BODY.

2 grms of pure perfectly white neutral body, freshly prepared, and possessing a melting point 38,5—39° C., were distilled. On melting, the neutral body gave a practically colourless liquid, which, as the temperature rose, coloured itself but very slightly. The whole distilled without any decomposition, beyond the merest traces towards the end of the destillation, at the temperature 241°. Paal[2] had given 235—240° C.

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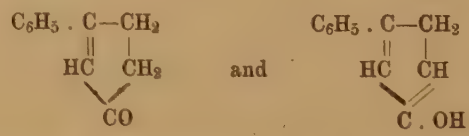
[1] Dissertation p. 17.
[2] Ber. 17, p. 913.

INVESTIGATION OF THE CHANGES WHICH THE NEUTRAL BODY EXPERIENCES, ON STANDING IN THE AIR, AND OVER SULPHURIC ACID.

Paal noticed that, on standing, his «Phenyl Methyl Furfuran» coloured itself and became liquid. Schloesser also found the body to be possessed of this property, and further discovered that the altered substance, in contradistinction to the original crystalline body, yielded a compound with Phenyl Hydrazin. He moreover noticed that the substance when placed over Sulphuric Acid in an exsiccator became liquid. Dietzel[1] discovered in Dimethyl-Ketopentene precisely similar properties. On standing it became coloured and more viscid, and then yielded a compound with Phenyl Hydrazin.

Fittig[2] having suggested that the two, according to his explanation of the method of production of the neutral body, theoretically possible formulae;



might be held as identical, and that the apparently spontaneous change of the crystalline body, incapable of yielding a compound with Phenyl Hydrazine, into one giving such a compound, might point to the correctness of this assumption, the investigation became one of great interest.

ATTEMPTS TO OBTAIN THE COMPOUND WITH PHENYL HYDRAZINE.

Two samples of the already altered substance, which had been actually prepared by Schloesser, but not as I take

[1] Ann. 250, p. 211.
[2] Ber. 21, p. 2137. Ann. 250, p. 176.

it, at one and the same time, on diluting with pure Ether, and treatment with Phenyl Hydrazin gave, in the one case, a small quantity of the compound (approx: 0,05 grms), and in the other, absolutely none. Of two samples, prepared by myself by the destillation of P a a l 's Acid, one (2,5 grms) which had been twice distilled with steam, failed, even after three weeks, to show the slightest colouring, whereas the second (4 grms), distilled but once with steam, gave a mere trace of the compound, the whole having become liquid in the time. These two samples were products of two quite distinct destillations of the acid.

12 grms: of pure neutral body were obtained, and a portion of the already altered substance, added. After three months though the greater part was liquid, there were still crystals of unaltered neutral body present. A portion, representing aboult three quarters of the whole, was treated with Phenyl Hydrazine, and mere traces of the sought for compound, obtained. The remainder was distilled with steam, and there passed over pure unaltered neutral body, and remained behind a resin, which on cooling became quite hard, powdered to a light brown powder, melting between 70—78° C., from which nothing was extracted by warming with Sodium Carbonate solution. All attempts to obtain from the resin a pure substance, failed. It was found possible to obtain from the portion treated with Phenyl Hydrazin, after binding the excess of the same with Hydrochloric Acid, a considerable quantity (3 grms) of Neutral Body. This recovered Neutral Body after standing five weeks in the air failed to show any colouring, or the slightest sign of becoming liquid.

THE NATURE OF THE CHANGE OVER SULPHURIC ACID.

These experiments were made with the sample, (p. 18 which after three weeks had remained unchanged. A portion was placed in a perfectly clean exsiccator over pure Sulphuric Acid. In four hours the substance had become considerably brown, and in twenty four hours was dark brown, and quite

moist. Eventually the whole became quite solid, and almost black in colour; in fact a hard resin. From this by destillation with steam, a very small quantity of unaltered neutral body was obtained, and the resinous mass when pulverised melted between the temperatures 70—80° C. Other portions of the name sample of Neutral Body were then placed over different drying agents, with the results,

over Phosphoric Anhydride no change observable after 14 hours,

over Calcium Chloride no change after the same length of time.

To prove that the rapid change over Sulphuric Acid was not due to impurities in the acid, the two following experiments were made.

A portion of the Neutral Body exposed over Calcium Chloride in an exsiccator, in which was a small vessel containing a solution of Sulphurous Acid, showed, even after twenty four hours, no tendency to change.

To a solution of Potassium Nitrite, in which some of the Neutral Body was suspended, sufficient Sulphuric Acid was added to evolve traces of Nitrous Acid. The experiment was made in a glas-stoppered cylinder. After many hours no change was noticeable, and only after considerable time did the Neutral Body become yellow and oily.

Several attempts were made with portions, which had been sexposed for longer or shorter times over Sulphuric Acid, to obtai any result with Phenyl Hydrazine, but always without success.

Experiments were then made trying the effect of the mineral acids upon the Neutral Body.

The Neutral Body suspended for six or seven days in pure concentrated Hydrochloric Acid, acquires a slight violet colour, but otherwise remains quite unchanged, and the ethereal solution of the recovered body gives no compound with Phenyl Hydrazine.

When added to pure concentrated Nitric Acid, a violent

reaction ensues, and Benzoic Acid crystallises out of the yellow pasty mass, obtained on diluting with water.

In concentrated Sulphuric Acid, the Neutral Body dissolves, and the solution possesses slight fluorescence.

From these experiments it may be concluded, that the Neutral Body is susceptible of a certain change, occasioned by what, is still uncertain, but most certainly influenced by the presence of extraneous matter. Moreover, that in some cases it is possible to obtain with Phenyl Hydrazine, a compound, but that the same is not always the case, nor would it seem, that from this fact, any support of the identity of the two theoretically possible formulae, as at first assumed, can be obtained.

EXPERIMENTS MADE WITH A VIEW TO DECIDE THE CONSTITUTION OF PHENYLKETOPENTENE.

ACTION OF HYDROBROMIC ACID ON THE NEUTRAL BODY.

A small quantity (0,5 grms) of the pure substance introduced into a clean dry glas-stoppered cylinder. About 5 cc fuming Hydrobromic Acid, freshly prepared, was then added, the cylinder being cooled by immersion in ice. The heat evolved was inconsiderable. The contents of the cylinder were shaken from time to time. At the end of two or three hours the Neutral Body had all dissolved, and the liquid become very dark in colour. The mixture was allowed to stand over night, and by morning, it was evident that considerable decomposition had taken place. Water was added, and the precipitated matter examined for Bromine by treatment with Sodium Amalgam on the water-bath, and subsequent examination of the liquid for the presence of a Bromide. No evidence of the presence of Bromine was obtained.

ACTION OF HYDROBROMIC ACID ON THE ACIDS OF PAAL AND SCHLOESSER.

The experiments were made in an exactly similar manner to the last one. In both cases the acid was recovered, showed the correct melting point, and no evidence of Hydrobromic Acid having had any action could be obtained.

ACTION OF SODIUM AMALGAM ON THE ACID OF PAAL.

0,5 grms of the acid of Paal was treated with Sodium Amalgam, care being taken to avoid the solution becoming too alkaline. On adding Hydrochloric Acid, the original quantity of the acid was recovered, unchanged in appearance, and showing the correct melting point, 178—179° C.

ACTION OF ACETIC ANHYDRIDE ON THE NEUTRAL BOBY.

0,5 grms pure Neutral Body was taken, and 3 grms Acetic Anhydride added. The two were heated together in a flask provided with a reflux condenser, for three quarters of an hour. After becoming quite cold, water was added, and then a crystal of the Neutral Body; the whole crystallised out unchanged. A precisely similar result was obtained with Acetyl Chloride.

TETRAHYDRO. PHENYL METHYL FURFURAN.

Paal[1] obtained this body by treating an alcoholic solution of the Neutral Body with Sodium. According to him, it contains four atoms more Hydrogen than the Neutral Body, and boils about 230° C. Moreover, the compound is, according to Paal, no alcohol, because it distils over Sodium, undecomposed.

With a view to investigating this body more completely, I prepared it after the following manner. 10 grms of Neutral

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[1] Ber. 17, p. 2756.

Body were dissolved in about 250 cc. Alcohol and treated with 23 grms. Sodium. This amount of Sodium corresponded to four times the theoretical quantity, and was found to give much better results than when only two to three times the theoretical quantity was used. The Sodium, after being weighed, was kept in absolute ether until required, and was added very gradually. The product, after separation from alcohol, was treated with dilute Hydrochloric Acid until slightly acid, and then shaken out with ether. After evaporating the ether, the body was distilled with steam, taken up with ether, and eventually fractionated. As a result of three fractionations it was found possible to obtain a portion (2 grms approx:) boiling constantly at 233° C. This was analysed with the following results.

I. . 2472 grms gave . 1982 H_2O and . 7397 CO_2.
II. . 1830 grms gave . 1483 H_2O and . 5464 CO_2.

	Calculated		Theoretical for $C_{11}H_{14}O$
	I.	II.	
H =	8,90	9,00	8,64
C =	81,59	81,43	81,48

It having been noticed that, in fractionating the above substance over Sodium, the latter was, in every case, attacked, it was determined to examine the action of Sodium on the body. A small quantity, about 0,5 of a gramme, was placed in a perfectly dry, small, narrow test-tube. The tube was closed with a well-fitting cork, through which passed a thin glass tube finely drawn out at the end. A small pellet of sodium was introduced into the liquid, and the tube heated in a Sulphuric Acid bath. The sodium was immediately attacked, and at 50° C. the gas evolution had become tolerably energetic. The liquid coloured itself dark brown, and there separated out a dark brown solid body, which eventually hindered the free action of the sodium. An exactly similar experiment was tried with the pure Neutral Body, but no trace of gas-evolution was noticeable, and the Neutral Body remained quite unacted upon.

In the hopes of being able to prepare an ether of the compound, the following experiment was made. 0,85 grms was

taken and dissolved in absolutely water-free toluenc which had been many times distilled over Sodium, and upon which the metal had no longer any action. Sodium was added in small strips until apparently no further action took place, and afterwards Benzoyl Chloride until a small excess of the same remained. After freeing the liquid from all unaltered Benzoyl Chloride, by lengthy shaking with a solution of Sodium Carbonate, and subsequent extraction with pure ether, the produc of the above reaction refused to yield a solid body.

As a second attempt, 1 grm of a fresh sample of the Hydrogen compound was heated with Acetic Anhydride, until the latter just began to distil, for something like half an hour, and after the lapse of this time, the unaltered Anhydride was distilled off, and the product fractionated. The thermometer showed no stationary point, and decomposition evidently accompanied the destillation.

0,5 grms of the Hydrogen compound was then heated with Benzoyl Chloride. The experiment was made in a small test tube, through the cork of which there passed a finely drawn out glass tube, which was bent downwards. The test-tube was heated in a Sulphuric Acid bath. At 35° C. the mixture assumed a light green tint, which darkened as the temperature rose, and the liquid eventually became quite brown. At 110° C. the evolution of Hydrochloric Acid was marked and only after half an hour had it ceased. The mixture was kept at this temperature for quite an hour longer, and subsequent raising of the temperature to 145° C. occasioned no further evolution of Hydrochloric Acid. As in the experiment recorded above, the excess Benzoyl Chloride which remained, was removed by lengthy shaking with a solution of Sodium Carbonate. The Benzoyl Chloride which had been freshly distilled, and showed a quite constant boiling point, was used in quantities slightly in excess of the theoretical, on the assumption the Hydrogen compound is an alcohol.

The following experiments were made with the liquid product.

A portion was boiled with a solution of pure Sodium Carbonate, and after removal of the still remaining oil, the solution was tested for Chlorine. Mere traces only were found, and on acidifying the solution no Benzoic Acid was precipitated. A second portion was heated with Caustic Potash. After removing the oil still remaining after heating with Caustic Potash, on acidifying, there resulted a copious precipitation of Benzoic Acid.

·1998 grms of the liquid was heated with pure Caustic Soda in a flask provided with an inverted condenser, on the water-bath for an hour. The oil still remaining was carefully removed with ether, and the solution acidified. The precipitated Benzoic Acid was extracted with ether, until further shaking out did not give the ether an acid reaction, nor did anything remain after evaporating off the ether. The acid so obtained was converted into its Calcium Salt, and the weight of the air-dried salt equalled ·0746 grm. This corresponds to a percentage of 23,32 Benzoyl (C_6H_5CO) in the body, instead of 39,47, the theoretical amount if the substance was a pure Benzoyl Ether.

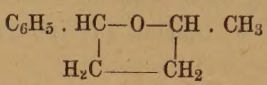
It may be that Benzoyl Chloride in addition to forming an ether, splits off water from the alcohol, and herein may lie the reason of the impurity of the product of the action between these two bodies.

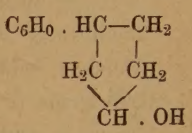
My time being limited, and all attempts to obtain a solid body having proved futile, the investigation was not carried further, but I hope at some future date to return to the same.

CONCLUSION.

Paal, as has already been stated, regards the Neutral Body and its derivatives as Furfuran compounds. The existence of a Hydride, containing four atoms of Hydrogen more than the Neutral Body, and distilling over Sodium, undecomposed,

rendered the assumption highly probable. According to Paal's interpretation the body was merely a Hydride of the Furfuran compound, Phenyl Methyl Furfuran; whereas, if the constitution proposed by Fittig were correct, the compound must be an alcohol.



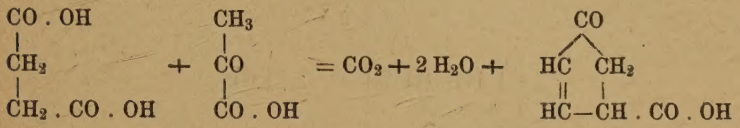


Viewed in the light of the experiments recorded above, the existence of a Hydrogen derivative containing four atoms of Hydrogen more than the Neutral Body is established, but the probability of its being an alcohol receives very great support. The only proof of the non-alcoholic nature of the body, that Paal adduced, was the possibility of distilling the compound over Sodium, undecomposed. However, as has been shown, the compound is attacked by Sodium, and with the pure body the action commences even in the cold. The evolution of Hydrochloric Acid on heating the substance with Benzoyl Chloride, and the formation of a body undecomposed by heating with a solution of Sodium Carbonate, but decomposed, with formation of Sodium Benzoate, on heating with Caustic Soda, seem to point to the possibility of obtaining a Benzoic Ether.

The failure of Nascent Hydrogen to act upon Paal's acid is in exact agreement with the result obtained by v. Eynern in the case of Metronic Acid. The dibasic acid, dehydro-mucic Acid readily takes up two atoms of Hydrogen, whereas neither the dibasic acid Methronic Acid, or Paal's Phenyl Methyl Furfuran Carboxylic Acid, show any tendency to combine with Hydrogen.

Again too, the behaviour of the acids of Schloesser and Paal with concentrated Hydrobromic Acid, accords very badly with the assumption that they are Furfuran bodies.

Quite recently Mr. Parker[1] has succeeded in obtaining as the result of the condensation taking place between Pyro-racemic Acid and Sodium Succinate, a new acid, $C_6H_6O_3$, whose method of formation is readily explained:



but for which, the assumption that the body is a Furfuran compound, affords no ready explanation.

When we consider that the strongest point adduced by Paal in favour of the Furfuran constitution, has fallen to the ground, and moreover, have regard to the many points in which the properties of the bodies fail to agree with the assumption of Paal, we are compelled to accept as the more likely constitution the one proposed by Fittig, although, as yet, it lacks absolute proof of its accuracy.

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[1] Ber. 22, 2104.

CURRICULUM VITAE.

Ich, Arthur Colefax, bin als einziger Sohn am 9. Juli 1866, in Bradford in England, geboren. Meinen Schulunterricht erhielt ich in der «Bradford Grammar School», woselbst ich neun Jahre verblieb. Die letzten zwei Jahre dieser Zeit gehörte ich der naturwissenschaftlichen Abtheilung dieser Schule an, mich besonders mit Chemie und Physik beschäftigend. Im Januar 1885 wurde ich zu «Lady Hartings Exhibitioner, Queen's College, Oxford», ernannt, trat aber nicht als solcher ein.

Im Juli desselben Jahres erhielt ich den Preis als «Natural Science Postmaster des Merton College, Oxford», und trat dort im Oktober desselben Jahres ein.

Nach dreijährigem Studium, welches hauptsächlich der Chemie galt, absolvirte ich mit dem ersten Grade in dem «Final Natural Science Examination».

Gleich darauf bezog ich die Kaiser-Wilhelms-Universität zu Strassburg, wo ich im Laboratorium des Herrn Professor Fittig die folgende wissenschaftliche Untersuchung ausführte.